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Effect of Water Content, Temperature and NaCl on CO_2 Corrosion of Carbon Steel (A106B) in Iraqi Crude Oil

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Abstract

An investigation was carried out to determine the corrosion rate of carbon steel (A 106 Grade B) as flow line in crude oil production with CO_2 content employing three Iraqi crude oil (Kirkuk crude oil, Halfaya crude oil, and Rumalia crude oil) with identical produced water (brine) [1%NaCl, 2%NaCl, and 3%NaCl]. Experiments were performed in an autoclave test apparatus, crude oil-produced water mixtures, water cuts were (0, 10, 20, 30, 40, and 100%), and temperature (20, 40, 60°C). For all experiments, CO_2 partial pressure was maintained at 4bar and rotational speed 500 rpm. The corrosion rates were determined by the weight loss method. The results revealed that the corrosion rate of carbon steel increased by increasing water cut and temperature, but decreased with increasing salt concentration for all types of crude oil. Rumaila crude oil exhibited the highest corrosion rate and Kirkuk crude oil exhibits the lowest corrosion rate while Halfaya crude oil exhibits a moderate corrosion rate.

Keywords: CO_2 corrosion, carbon steel, crude oil, water cut, produced water, autoclave.

تاثير المحتوى المائي، درجة الحرارة، وتركيز Nacl على تاكل غاز CO_2 للفولاذ الكاربوني (A 106 B) في النفط الخام العراقي

الخلاصة

إن الدراسة الحالية تركز على دراسة معدل التأكل للصلب الكربوني في خطوط الانابيب المستخدمة في نقل النفط الخام بوجود غاز ثاني اوكسيد الكربون باستخدام ثلاثة نفوط خام عراقية (نفط خام كركوك ونفط خام حلفاية ونفط خام الرميلة) مع تماثل الماء المنتج (1%كلوريد الصوديوم و 2%كلوريد الصوديوم و 3% كلوريد الصوديوم). ان دراسة تأكلية النفط الخام العراقي تتم لاول مرة في هذه الاطروحة. تم إجراء التجارب في وعاء ضغط مغلق، واستخدمت خلائط من (النفط الخام –الماء المنتج) وكانت نسب الماء المستخدمة (0 و10و 20 و30و 40 و100,%) وكان حجم الخليط في جميع التجارب 100مل وبدرجات حرارة (20 و40 و60 درجة مئوية). في جميع التجارب تم تثبيت الضغط 4 بار وسرعة دوران 500 دورة بالدقيقة. تم إيجاد معدلات التأكل بطريقة الفقدان بالوزن. أظهرت النتائج أن معدلات التاكل في الصلب الكربوني تزداد بزيادة نسبة الماء وكذلك بزيادة درجة الحرارة ولكنها تتناقص بزيادة تركيز الملح ولجميع انواع النفوط. كذلك أظهرت النتائج ان النفوط المختلفة لها تأثيرات مختلفة على تاكل الصلب الكربوني حيث أظهر نفط خام الرميلة أعلى معدل تأكل في حين أظهر نفط خام كركوك أوطا معدل تأكل ونفط خام حلفاية أظهر معدل تأكل متوسط.

الكلمات الدالة: تاكل CO_2, الصلب الكربوني, النفط الخام, نسبة الماء , الماء المنتج, اوتوكلف.

Introduction

Internal corrosion of carbon steel pipelines occurring in the presence of CO_2 is a substantial problem in the oil and gas industries. It is generally occurring with the presence of free water, the increase of the volume fraction of water phase will increase the probability of corrosion. As the produced

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water level increases, the corrosion rates of carbon steel increase very rapidly and causes damage of petroleum and gas pipelines [1]. There are many factors that affecting metal corrosion, some of these are the properties of water, crude oil kind, water-to-oil volume, temperature and carbon steel type [2]. Carbon steel is generally used in the petroleum industry for transportation of crude oils and gases from production sites to different refining platforms. The flow lines and pipelines made from carbon steel are subjected to internal corrosion due to CO_2 and other environments [3]. Carbon dioxide corrosion, also called as" sweet corrosion" is a significant problem in oil and gas industry. Extensive essays have been conducted on the effect of inorganic dissolved salts and gases on the corrosion of carbon steel in crude oil environments, but the effect of the actual crude oil is generally either ignored or supposed to be substantially unimportant.

Tests for corrosion which are guided on carbon steel in the absence of crude oil (brine only) do not give a precise consequence of the behavior of carbon steel in the oilfields. This is particularly true for electrochemical tests, which require the high conductivity of water phase for accuracy. Therefore, the results of such tests cannot be depended to estimate the corrosion problem and the effect of inhibitors in crude oil production [4]. Hence, the test environment data that resembles the production systems of crude oil should contain the actual crude oil, artificial produced water similar to that of oilfield and a gas phase, if the test is to produce valid results [5]. Different crude oil has significant effects on carbon steel corrosion [6]. The present work focuses on investigating the effect of different parameters on the CO_2 corrosion rates of carbon steel pipes that are used as flow lines in three different Iraqi crude oil under field condition and the effect of water cut in crude oil on its corrosivity.

Experimental Procedure

The corrosion experiments were carried out in 250ml stainless steel autoclave. A picture of autoclave and experimental setup is shown in Figure (1).

Three Iraqi crude oils were used in the experiments (Kirkuk crude oil, and Rumaila crude oil, Halfya crude oil), the physical properties of crude oils is listed in Table 1. The analysis was carried out in the North Refineries Company laboratory and North Rumalia.

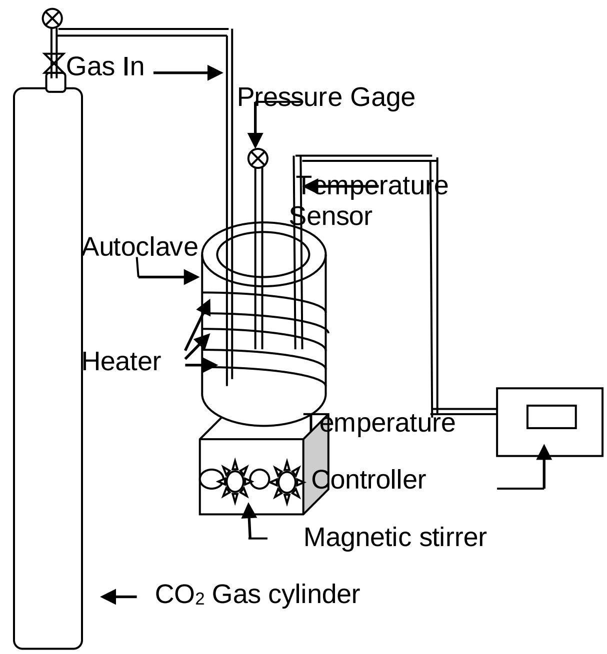

Fig. 1. Schematic of test apparatus

Table 1. The physical properties of crude oil

Properties	Fields		
	Kirkuk	Halfaya	Rumalia
API	36.2	24	33
B.S & W (vol %)	trace	0.75	0.75
Salt cont.(mg/L)	11	12	23
Sulfur (wt. %)	2	2.92	3.9
Vanadium (ppm)	41	53.3	43
H_2S cont. (ppm)	11.7	1	1.1
Nickel (ppm)	15	11	8.2
SP.gravity at 15.6°C	0.8437	0.8851	0.8772
Carbon residue (wt.%)	3.4	8.9	7.3
conductivity	0	0	0

Identical produced water (brine) (1% NaCl, 2% NaCl, and 3% NaCl), water cuts were (0, 10,20,30,40 and 100%) and total volume of mixtures inside the autoclave was always kept at 100ml and temperature (20, 40, and 60°C). For all experiments, CO_2 partial pressure was maintained at 4 bar and rotational speed 500 rpm. The corrosion rates were determined by the weight loss method.

The material used as a specimen was cut from carbon steel pipe (A 106 Grade B). The typical chemical composition of the carbon steel is listed in Table (2). Analysis of carbon steel was carried out by using spectrotest apparatus at college of engineering in Basra University.

Table 2. Chemical composition of carbon steel (A 106 grade B)

Comp.	C	Mn	P	S
Wt %	0.06	0.34	0.033	0.04
Cu	pb	Si	Al	Fe
0.057	0.01	0.01	0.01	99.4

Before each experiment, one specimen was abraded in sequence under running tap water by using emery paper of grade number 80, 220, 400, 600, and 1000 respectively, washed in distilled water, dried with clean tissue, immersed in acetone and dried with clean tissue, immersed in benzene and dried with clean tissue, and dried with an air blower, then kept in desiccators over silica gel until use. Depending on the water cut selected for the test. Crude oil and brine were placed together in a beaker and stirred for 3hrs in order to form an emulsion, then the emulsion was transferred to the autoclave and deoxygenated with CO_2 gas for 1hr. Weighing the specimen and record W1, then the specimen was suspended into the autoclave, closing the autoclave, and CO_2 gas was injected providing no leaking occur. Turn on the temperature controller and set it to the required temperature, a magnetic stirrer was used to stir the emulsion at a rotational speed of 500 rpm; stirring was maintained during the test 24hrs to get a homogenous mixture. Once the temperature reached to the desired value the test period started. After each test, the specimen was removed from the autoclave and cleaned chemically by putting it in a cleaning solution (500 mL 35% HCl +3.5 g hexamethylene tetramine +500 mL distilled water) and treated with vigorous stirring at room temperature for (10–25) minutes. The treated coupon was removed, rinsed with de- ionized water, cleaned with a soft brush. The specimen was washed with water and then immersed in acetone, then dried and weight. The weight loss was converted to give the corrosion rate by the formula:

MPY=534W/DAT
MPY: mils per year
W: weight loss in milligrams.
D: density in grams per cubic centimeter.
A: area in square inches.
T: time in hours. And
1 mpy = 0.0254 $\frac{mm}{yr}$

Results and Discussion

The corrosion rate was plotted against water cut, temperature, and salt concentration for all types of crude oil.

Effect of Water Cut on CO_2 Corrosion of Carbon Steel in Three Iraqi Crude Oil

The increase of water cut in the mixture results in a significant increase in the corrosion rate of carbon steel. Figures (2) to (4) illustrate the effect of water cut on corrosion rate of carbon steel, at 60°C, pressure 4bar, and salt concentration 1%NaCl, 2%NaCl, and 3%NaCl in Kirkuk crude oil, Rumaila crude oil and Halfaya crude oil respectively.

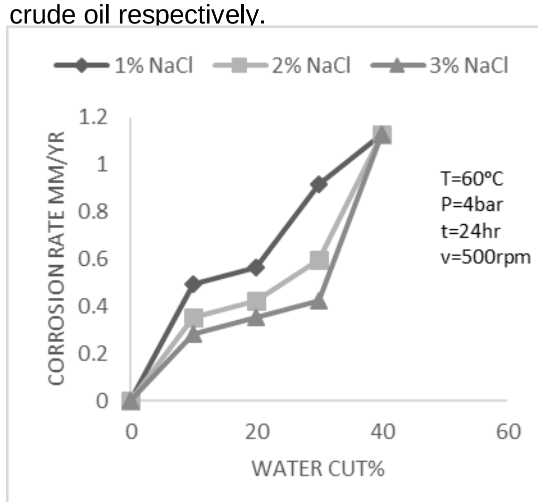

Fig. 2. Effect of water cut on corrosion of carbon steel in (Kirkuk crude oil/ brine/ CO_2) mixtures

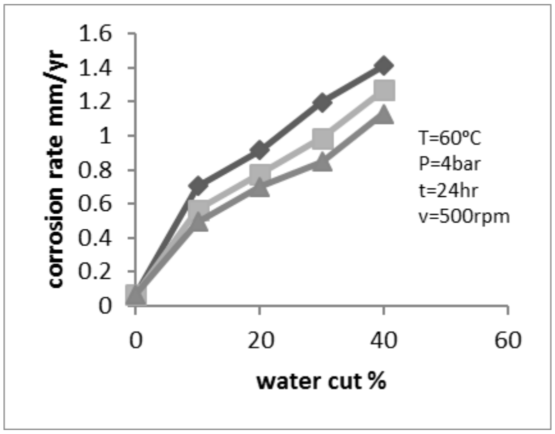

Fig.3. Effect of water cut on corrosion of carbon steel in (Rumaila crude oil/brine/CO_2)

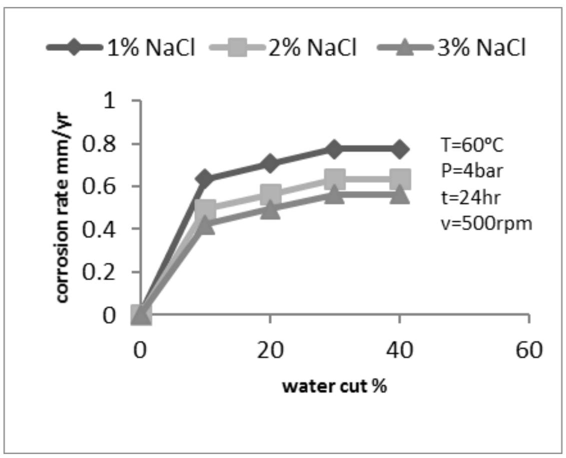

Fig.4. Effect of water cut on corrosion of carbon steel in (Halfya)

For Kirkuk crude oil, with all salt concentration, it can be observed that there was no symptom of corrosion overtake with 0% water cut. The corrosion rate increased abruptly by increasing water cut from 0% to 10% , whereas it increased slightly when the water cut increased from 10% to 30% . However it was increased abruptly once more with increasing water cut to 40%.

It is important to note that even at low water cuts (10% and 20%), the corrosion rate was not negligible for example (at 10% water cut, 1%NaCl the corrosion rate is 0.493 mm/yr). Also, it can be observed that at 40% water cut, the corrosion rate reached the value (1.12776 mm/yr) for all salt concentrations [1% NaCl, 2% NaCl, and 3% NaCl].

For Rumaila crude oil, it can be observed that the corrosion rate at 0%water cut (crude oil only) was 0.07 mm/yr. For all salt concentration the corrosion rate increased abruptly by increasing water cut from 0% to 10%, At water cut from 10% to 40% the corrosion rate increased gradually.

For Halfya crude oil, it can be observed that there was no symptom of corrosion attack at 0% water cut. For all salt concentration the corrosion rate increased abruptly by increasing water cut from 0% to 10%. At water cut from 10% to 30% the corrosion rate increased gradually. Also it can be observed that there was no change in corrosion rate beyond 30% water cut up to 40% water cut.The reason of this behavior is that the API of this crude oil is 24. Therefore, it regards (medium crude oil) the emulsion viscosity increases with increasing water cut, the increasing viscosity inhibit the mass transfer in the mixture.

The corrosion rates increase with increasing water cut due to the corresponding increase in CO_2 which increase the formation of H_2CO_3 and accelerates CO_2 corrosion reaction [2], Equation (1) shows the initial step in this reaction:

On account of this state, it is linked with three cathodic reactions and one anodic reaction. The cathodic reactions involved, first the reduction of carbonic acid into bicarbonate ions Equation (2), second the reduction of bicarbonate into carbonate ions Equation (3), and third the reduction of hydrogen ions Equation (4).

$CO_2 + H_2O \rightarrow H_2CO_3$ ……………..………. (1)

$H_2CO_3{}^{-} \rightarrow H^+ + 2HCO_3^-$ …………......(2)

$HCO_3^- \rightarrow H^+ + CO_3^{-2}$ ………………..…….. (3)

$2H^+ + 2e^- \rightarrow H_2$ ………………...…………(4)

The corrosion product is just Fe^{+2} under the above conditions because CO_2 corrosion occurs under anaerobic condition so the oxidation reaction needed for the formation of ferric Fe^{+3} which was not included in Equation (5).

$Fe \rightarrow Fe^{+2} + 2e^-$ …………………………(5)

The increment of CO_2 in water confirms the processes of reactions (1),(2),(3) ,(4) and (5).

Comparison of the Corrosion Rates of Carbon Steel in Three Iraqi Crude Oil/Produced Water Mixtures

Crude oils from variant fields have different characteristics [7]. Corrosion affected markedly by the type of crude oil used in the presence of water[6]. Figures 5, 6, and 7 illustrate the behavior of three Iraqi crude oils with identical produced water (1% NaCl, 2% NaCl, and 3%NaCl) respectively. From figures 5, 6 and 7 we can classify the behavior of the crude oils into three types:

Type 1: In Rumaila crude oil the corrosion rate rapidly increases at a produced water level less than 10%. This type of behavior most risky one from the corrosion point of view, because of the high corrosion rate in spite of low level of produced water indicating that this is due to the kind of crude oil due to high concentration of salt with respect to others crude oil.

Type 2: In Kirkuk crude oil the corrosion rate increases progressively from (10% to 30%) water cut followed by rapid increase in corrosion rate in higher produced water level (40%) water cut.

Type 3: In Halfaya crude oil the corrosion rate increases gradually for the whole range of produced water level and then becomes more constant. This behavior is expected because Halfaya crude oil is the heavier oil with respect to other crude oil. Rumaila crude oil exhibits the highest corrosion rate and Kirkuk crude oil exhibits the lowest corrosion rate while Halfaya crude oil exhibits a moderate corrosion rate. This is attributed to:

1- The geographic location of the field.
2- The geological formation of the crude oil.
3-The physical properties of crude oil.

Also, it can be observed that the corrosion product (productive layer) that covers the surface of carbon steel immersed in Kirkuk crude oil is very difficult to remove comparing with the layer formed on the surface of samples that immersed in Halfaya crude oil and Rumaila crude oil.

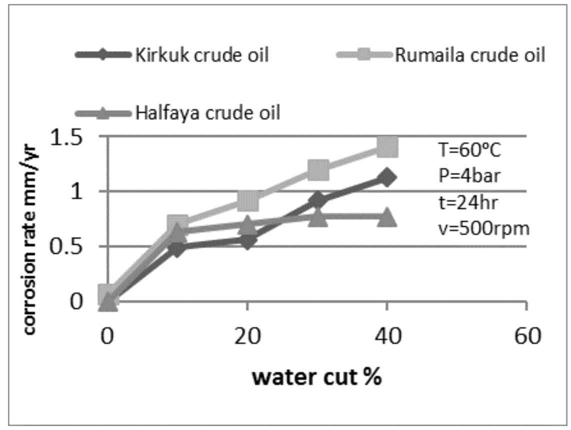

Fig. 5. Comparison of the corrosion rates of carbon steel in three Iraqi crude oil/produced water, 1% NaCl.

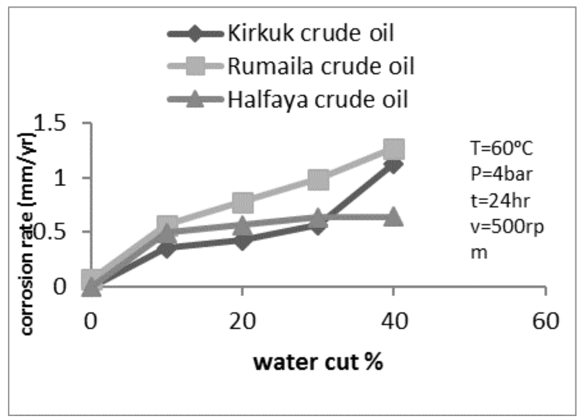

Fig. 6. Comparison of the corrosion rates of carbon steel in three Iraqi crude oil/produced water, 2% NaCl

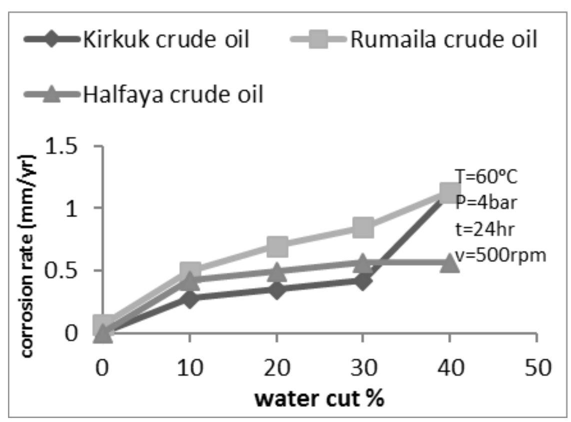

Fig. 7. Comparison of the corrosion rates of carbon steel in three Iraqi crude oil/produced water, 3

Effect of Temperature on CO_2 Corrosion of Carbon Steel in Iraqi Crude Oil

Figures 8, 9 and 10 shows the effect of temperature on CO_2 corrosion of carbon steel at 20% water cut, temperature 20, 40 and 60°C, carbon dioxide partial pressure 4 bar and salt concentration 1%NaCl, 2%NaCl, and 3%NaCl in Kirkuk crude oil, Rumaila crude oil and Halfaya crude oil respectively.

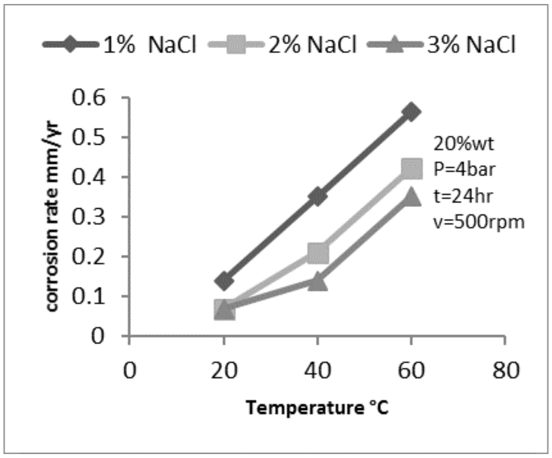

Fig.8. Effect of temperature on CO_2 corrosion of carbon steel in Kirkuk crude oil /brine

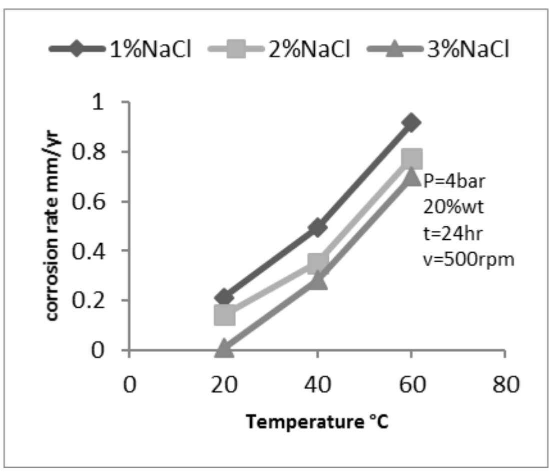

Fig.9. Effect of temperature on CO_2 corrosion of carbon steel in Rumaila crude oil /brine

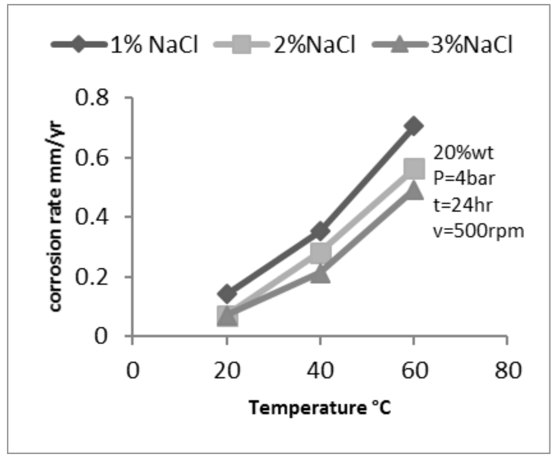

Fig.10. Effect of temperature on CO_2 corrosion of carbon steel in Halfaya crude oil /brine

It can be observed that the corrosion rate increases with the increase in temperature for example at 1% NaCl, Kirkuk crude oil, the corrosion rate changed from 0.14 mm/yr at 20°C to 0.352 mm/yr at 40°C and then increased to 0.564 mm/yr at 60°C the increasing temperature of the mixture can quicken the mass transfer process by decreasing the viscosity of the mixture[8]. An increasing of temperature with decreasing viscosity lead to accelerate the kinetics of CO_2 corrosion. On the other hand, the protective film of corrosion product ($FeCO_3$) decreases with increasing temperature.

Effect of Salt Concentration on CO_2 Corrosion of Carbon Steel in Iraqi Crude Oil

The corrosion rate of carbon steel in presence of CO_2 decreases with increasing of NaCl concentrations. Figures 11, 12 and 13 shows the effect of salt concentration on CO_2 corrosion of carbon steel in Kirkuk crude oil Rumaila crude oil, and Halfaya crude oil respectively at temperature 60°C and pressure 4 bar.

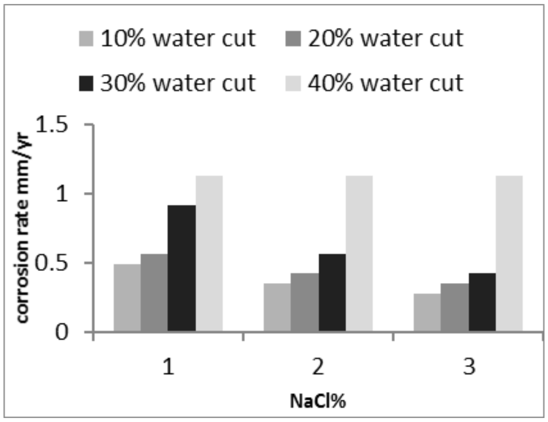

Fig.11. Effect of salt concentration on CO_2 corrosion of carbon steel in Kirkuk crude oil/ brine

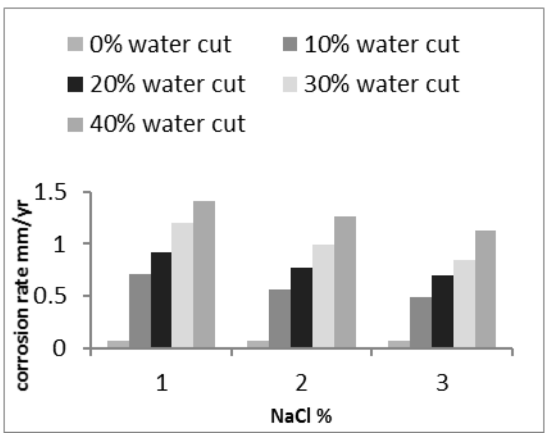

Fig.12. Effect of salt concentration on CO_2 corrosion of carbon steel in Rumaila crude oil

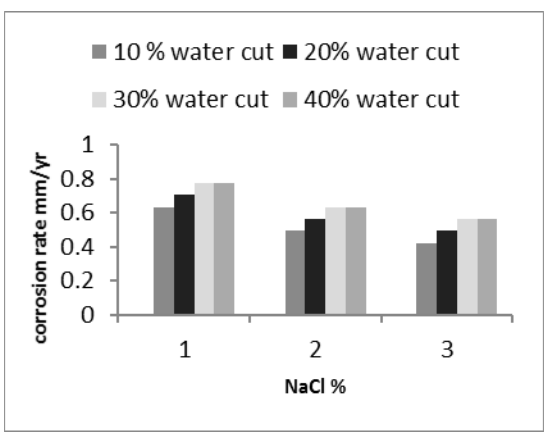

Fig.13. Effect of salt concentration on CO_2 corrosion of carbon steel in Halfaya crude oil

The causes of decreasing corrosion rate with increasing salt concentration in presence of CO_2 is that increasing the concentration of dissolved NaCl in mixture (emulsion) directly reduce the solubility of CO2 [9]. Regarding the effect of NaCl towards solubility of CO_2, it can be concluded that the solubility of CO_2 in NaCl solution tends to affect the kinetics of corrosion [10]. The cathodic reaction of corrosion decreases when the solubility of CO_2 decreases [8,11]. Cathodic reaction of CO_2 corrosion is shown in Equations 2, 3, 4.

Depending on the clarifications above, it can be inferred that decreasing corrosion rate of carbon steel, with salt concentration 1%, 2%, and 3% NaCl in presence of CO_2, is caused by: first, salt retarding factor. This factor is one of the properties of dissolved salts in the mixture which could impede anodic reactions and cathodic reactions. Increasing the dissolved salts content lead to an increase the viscosity and density of the mixture (emulsion) which in turn inhibit, both mass and ion transfer [12] and decrease the corrosion rate. Second, interfacial tension factor. Interfacial tension factor is a significant factor in oil – water two phase by influencing flow patterns. If oil – water interfacial tension value is low, it lowers the threshold for which water can be entrained by the oil as a dispersed flow and oil water will flow as a dispersed flow (low corrosion rate). On contrary, if oil-water interfacial tension value is high oil and water have more tendency to be separated (high corrosion rate). The interfacial tension decreases with the increases sodium chloride (NaCl %) concentration [13]. Concerning the above reasons, the corrosion rate of carbon steel decreased with increasing salt concentration in mixture (crude oil/brine/CO_2).

Corrosion Rates of Carbon Steel in 100% Water Cut (brine/ CO_2)

Figure 14 shows the corrosion rates of carbon steel in 100% water cut at salt concentration (1% NaCl, 2%NaCl, and 3% NaCl), temperature (20, 40, and 60°C) and carbon dioxide partial pressure 4bar.

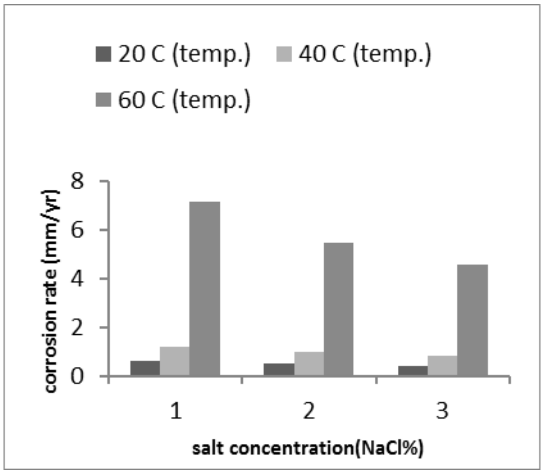

Fig.14. Effect of salt concentration on CO_2 corrosion of carbon steel in 100% water cut (brine)

It can be observed that increasing salt concentration significantly decreases the corrosion rate of carbon steel. The corrosion rate decreased from 7.1197mm/yr at 1% NaCl to 5.427mm/yr at 2% NaCl and then decreased to 4.58mm/yr at 3%NaCl.

Comparison of the Corrosion Rates of Carbon Steel in (Brine/CO_2) Mixtures and (Crude Oil/Brine/CO_2) Mixtures

It is obvious from Figures 15, 16, and 17 that there is a difference in corrosion rates of carbon steel in (brine/CO_2) mixture and (crude oils/brine/CO_2). Without the oil phase, 100% water cut (brine/CO_2) the corrosion rate of carbon steel is the highest, the presence of crude oil decreases the corrosion rates. This can be attributed to the fact that the corrosion product formed on the surface of metal plays an intensive role on CO_2 corrosion. Therefore, the presence of crude oil leads to the formation a thick layer on the surface of carbon steel which is predominantly ($FeCO_3$) which could act as protective layer, whereas in the absence of crude oil (100%) water cut, the surface of carbon steel covered with a light film which is easily removed.

Corrosion tests that are used to predict corrosion rate of materials in laboratory tests in the absence of crude oil give higher corrosion rate than it is found in oilfield production [14]. This can be attributed to the fact that crude oil act as natural inhibitor in oilfield production and when mixed with water it forms barrier between metal surface and water. In addition, the present of some components in the crude oil (oxygen, sulfur and nitrogen) has a direct inhibitor of corrosion, these components which can adsorb to the steel surface either from the oil phase or from the water phase after spliting to give corrosion production [15].

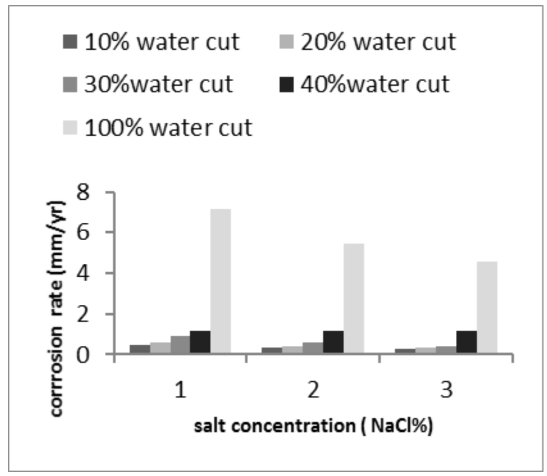

Fig.15. Comparison of the corrosion rates of carbon steel in (brine/CO_2) mixtures and (Kirkuk crude oil/brine/CO_2) mixtures at salt concentration 1%NaCl, 2%NaCl, and 3% NaCl

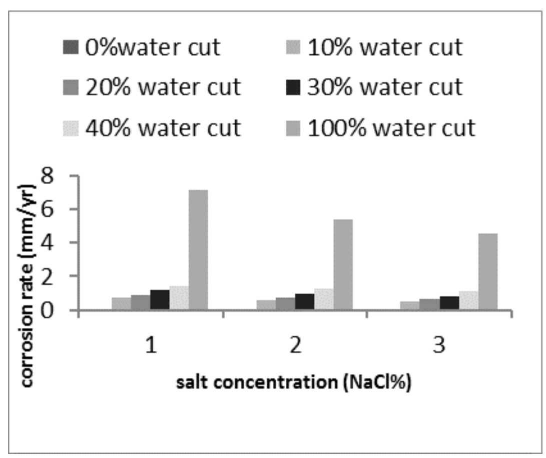

Fig.16. Comparison of the corrosion rates of carbon steel in (brine/CO_2) mixtures and (Rumaila crude oil/brine/CO_2) mixtures at salt concentration 1%NaCl, 2%NaCl, and 3% NaCl

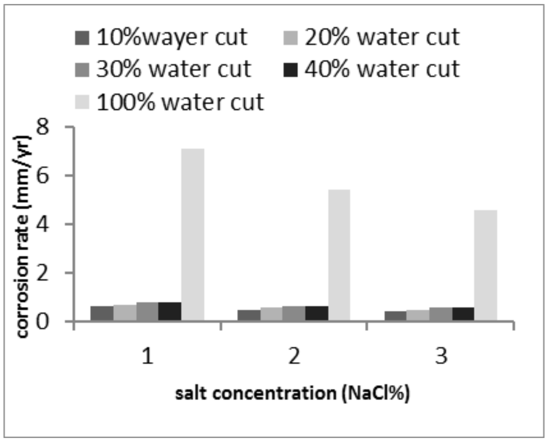

Fig.17. Comparison of the corrosion rates of carbon steel in (brine/CO_2) mixtures and (Halfaya crude oil/brine/CO_2) mixtures at salt concentration 1%NaCl, 2%NaCl, and 3% NaCl

Conclusions

1-Crude oil has a significant effect of the CO_2 corrosion of carbon steel in crude oil/brine mixture.

2-At 100% water cut the corrosion rate of carbon steel is the highest,

3-Rumaila crude oil exhibits the highest corrosion rate and Kirkuk crude oil exhibits the lowest corrosion rate while Halfaya crude oil exhibits a moderate corrosion rate.

4- Increasing of temperature results in an increase of corrosion rate under the condition used in this study.

5-Increasing the dissolved salt content reduce the solubility of CO_2 and lead to an increase of the viscosity and density of the mixture (emulsion) which in turn inhibit, both mass and ion transfer and decrease of corrosion rate and also the interfacial tension decreases with the increases of sodium chloride concentration which lower the corrosion rate.

6-The present of some components in crude oil (oxygen, sulfur and nitrogen) has a direct inhibiter of corrosion rate which can be adsorb to the steel surface to give corrosion product.

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